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Intermediate to long term optimization of dead-end ultrafiltration

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Document Version

Publisher's PDF, also known as Version of record

Publication date:

2007

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Zondervan, E. (2007). *Intermediate to long term optimization of dead-end ultrafiltration*. s.n.

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Chapter 4

Characterization of membrane fouling

In this chapter results of an autopsy performed on a PES (Poly Ether Sulphone) ultrafiltration membrane that was operated with surface water in a pilot over a six month period are presented. The outcome of the membrane autopsy showed that fouling present on the membrane surface is a complex mixture of polysaccharides, silica, organic industrial or urban waste such as alkyl-benzenes, phthalates and plant materials. By studying feed, permeate, backwash concentrate and cleaning concentrates during the operation period of the pilot, it could be concluded that especially silica, iron and organic content, tested as DOC (Dissolved Organic Content) and TOC (Total Organic Content) are retained on the membrane surface. This is in good agreement with the autopsy data.

4.1 Introduction

Better understanding of fouling may lead to improved fouling prevention techniques [1; 2]. The main objective of this chapter is to determine, in a qualitative way, which surface water components are retained on the membrane surface and cause fouling.

As stated in chapter 2, surface water can basically be divided into three types of potential fouling categories: 1) organic content, 2) inorganic content and 3) microbial content. Sometimes a fourth category may be added:

colloidal content. The organic content of surface water is often addressed as NOM (Natural Organic Matter) which is the collective name for humic- and fulvic acids. Several studies [3; 4; 5; 6; 7; 8] have shown that interactions, such as physical bridging and electro-static (van der Waals) repulsion occur between organic content and inorganic content (metal ions) and contribute significantly to membrane fouling. However, other work [10; 11] shows that microbial activity may result in membrane fouling, as microorganisms attach to the membrane surface and secrete extra cellular poly saccharides, forming a protective layer around the microorganisms.

4.2 Materials and methods

4.2.1 The 4 Inch ultrafiltration pilot

In this research a 4 Inch Norit-Xiga PES ultrafiltration module with a membrane surface of 6.0 m^2 was operated over a six month period. Surface water was pre-treated with a 200 micron pre-filter, before it was processed in the pilot setup. Pre-filtered feed water was filtrated in dead-end mode over the membrane module with an operating flux of $50\text{ l.h.}^{-1}.\text{m}^{-2}$ during 20 minutes. During filtration, flocculant was added to the feed water with a concentration of 1.0 ppm Al^{3+} (Quadrafluc PUS, ViVo Chem B.V.). After a filtration run, a backwash was performed at an operating flux of $200\text{ l.h.}^{-1}.\text{m}^{-2}$ during 2 minutes. When the trans-membrane pressure exceeded an upper limit of 0.3 bar, the membrane was cleaned by means of chemicals. First the membrane was cleaned with hydrochloric acid (0.1 mol.l^{-1}), for a period of 5 minutes flushing and 5 minutes soaking. In a second cleaning step a caustic cleaning with sodium hydroxide (0.1 mol.l^{-1}) was performed, flushing and soaking also lasted 5 minutes. The trans-membrane pressure and temperature were measured with pressure- and temperature indicators, filtration flux and backwash flux were regulated with pumps and flow controllers. The setup was connected via an interface (National Instruments) to a personal computer which was used to collect operational data. MEFIAS (Vito, Belgium) software was used to control the pilot. In figure 4.1 a simplified representation of the setup is presented. A photographic view of the pilot can be seen in figures 4.2 and 4.3.

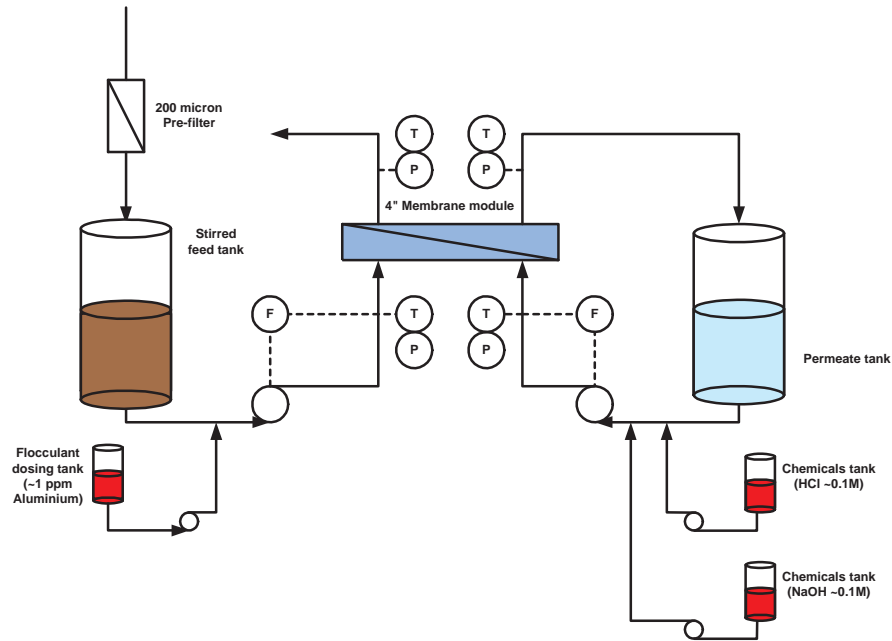


Figure 4.1: Simplified representation of the 4 Inch Pilot setup.

4.2.2 Characterization

Two sample sessions were performed during operation of the pilot (A four week period between both sample sessions), where feedwater, permeate, backwash concentrate and chemical cleaning concentrate (acidic- as well as caustic) were analyzed at the Vitens Laboratory for inorganic content (calcium, magnesium, silica, iron and aluminum, nitrate, nitrite, chlorine, ortho-phosphate, sulphate and ammonium), organic content (UV254, total organic content and dissolved organic content) and overall feed water quality (pH, turbidity and conductivity).

To characterize the fouling, a membrane autopsy was conducted in collaboration with the Université de Poitiers by means of FTIR, UV, C/N-analysis, pyrochromatography and thermolysis. The module was opened and two sample sets of fibers were cut out, one on the outside of the module and one at the center of the module. Material was isolated from fouled membrane fibers using sonication in MilliQ water, followed by lyophilisation. Part of the fibers were used for SEM photography at the Wetsus center for sustainable water technology.

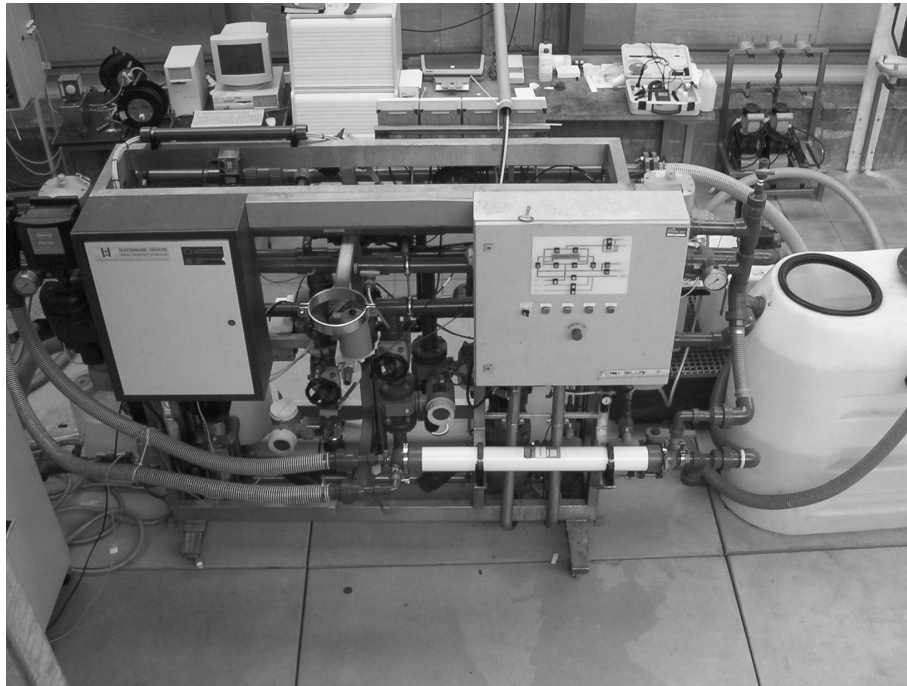


Figure 4.2: 4 Inch pilot setup, front view of the setup with in the center the membrane module and permeate tank at right hand side.

4.3 Results and discussion

4.3.1 Autopsy

SEM photography

SEM-pictures of fibers are shown in Figure 4.4. Algae were found during SEM photography, in the upper left figure a diatom is shown. Also bacteria were present (lower left and center figure). The lower right figures show fouling deposited on the membrane surface. It is noted that the fouling appears to be loosely deposited on the surface, this could be due to drying and heating of the fibers during the SEM photography.



Figure 4.3: 4 Inch pilot setup, back view of the setup with chemicals dosing system and feed tank (in the back).

Table 4.1: Carbon and Nitrogen content found on the fibers. (In 100 ml. milliQ water)

	DOC ($mg.l^{-1}$)	TN ($kg.l^{-1}$)	C/N
sample 1	3.81 +/- 0.08	0.04 +/- 0.01	95
sample 2	0.22 +/- 0.02	0.03 +/- 0.01	6.6

Carbon and nitrogen content

The C/N ratio is a frequently used indicator to quantify the nature of the deposit. It is well known that the higher the hydrophilic character of the NOM, the higher the nitrogen content and the lower the C/N ratio. Typical C/N ratios range from 4 -5 to more than 20 progressing from hydrophilic to hydrophobic NOM fractions. The two isolates showed very different carbon content, but similar nitrogen content, and consequently different C/N ratios. The possible difference in the data may be a result of the original location of the fibers in the module, where one sample was taken at the outside of the module and one sample was taken at the center of the module.

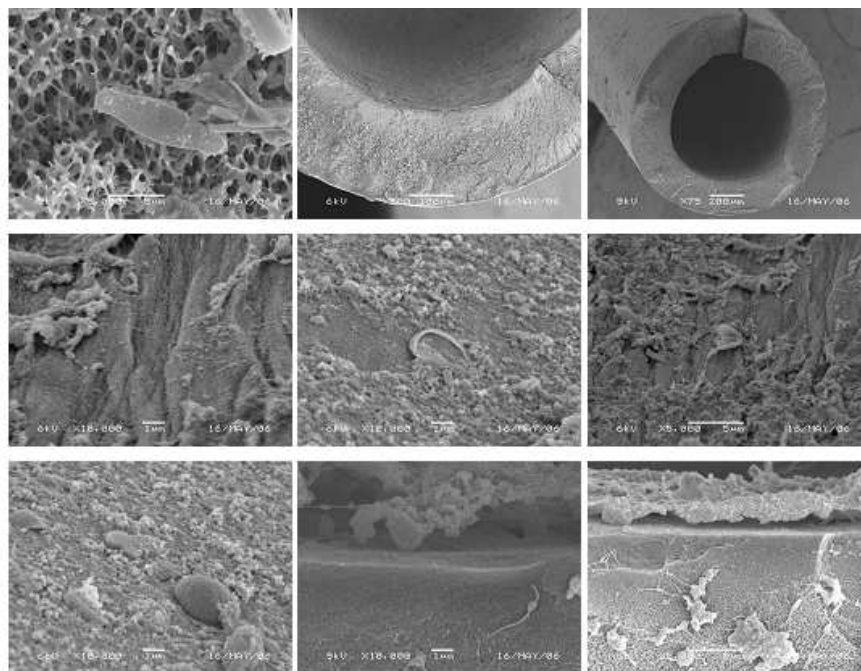


Figure 4.4: SEM photographs of the membrane. (Magnifications of $75\times$ to $10,000\times$)

High pressure size-exclusion chromatography (HPSEC) analysis

In figure 4.5 the HPSEC/UV spectrum is presented. The peak at $t=6.5$ minutes corresponds to high molecular weight proteins and polysaccharides. The broader band between 8 and 10 minutes may correspond to the presence of a higher proportion of high molecular weight structures. Both samples show peaks at similar wavelengths. Also the peak heights are similar, indicating that similar quantities of the components were present in the samples.

FT-IR analysis

FT-IR analysis can be used as a qualitative technique to identify fouling components. Results obtained for the FT-IR analysis, shown in figure 4.6, clearly indicate the presence of silica (clay mineral) with the major band at 1100 cm^{-1} associated with the one at 470 cm^{-1} . The large silica band may have overlapped with the characteristic band of sugars ($1000\text{--}1100\text{ cm}^{-1}$).

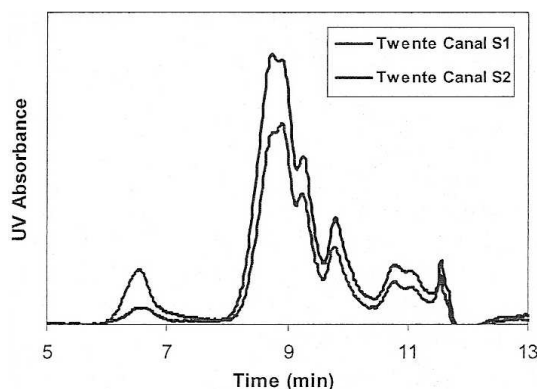


Figure 4.5: HPSEC/UV-260 of isolated foulants.

The band at 1650 cm^{-1} is also significant and again may indicate the presence of proteinaceous material. The large OH stretch at 3400 cm^{-1} may indicate adsorbed water as well as organic hydroxyl groups. Both samples show peaks at the same wavelengths, indicating good reproducibility.

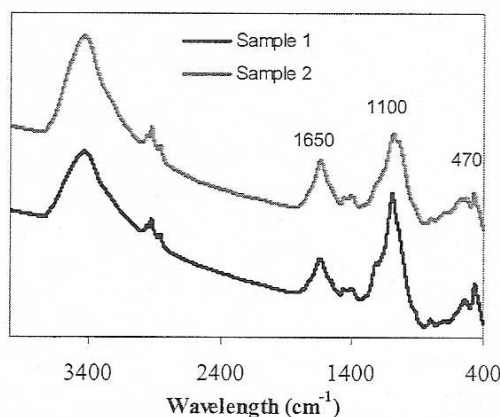


Figure 4.6: FT-IR spectra of the Twente Canal isolates.

Pyrolysis GC/MS

At high temperature, natural biopolymers and synthetic polymers are degraded to low-molecular-weight thermal decomposition products that are volatile enough to be separated and identified by GC/MS. The recorded pyrochromatogram, shown in figure 4.7, is dominated by the presence of

branched alkyl benzenes.

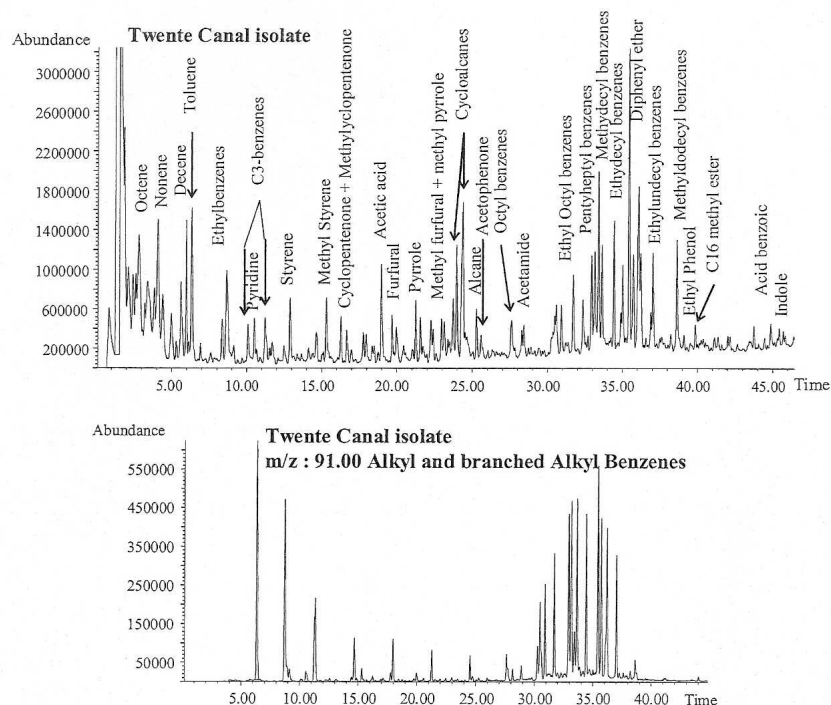


Figure 4.7: Pyrochromatogram of the Twente canal isolate (total ion current and m/z 91 chromatograms).

Clay minerals, as found in the FT-IR analysis of the samples, accumulated at the membrane surface and contained probably contaminated branched alkyl benzenes which strongly adsorb onto their surface.

Thermochemolysis GC/MS

The chromatogram of thermolysis of the fouling is shown in figure 4.8. The major observation in the thermo-chromatogram is that the Twente canal water incorporates heavier fatty acids up to C26. The presence of C15 iso and C15 anteiso fatty acids is a strong indicator of bacterial input. The longer chain fatty acids originate most probably from plant materials potentially adsorbed onto clay materials identified at the membrane surface. The presence of propenoic acid confirms the presence of plant materials, for example lignin derivatives in the fouling material. The peak for dimethyl phthalate

reinforces the hypothesis of industrial and/or urban contamination of the Twente canal.

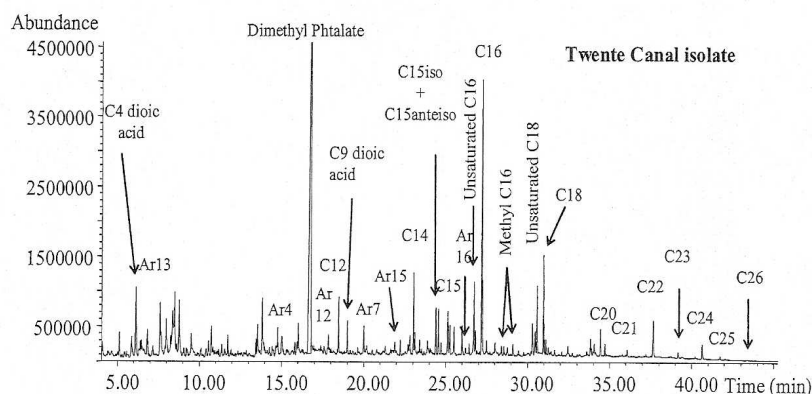


Figure 4.8: Thermochemolysis - TMAH/GC-MS chromatograms of the hollow fiber foulants (end). (Ar1: Benzaldehyde, 4-methoxy; Ar2: Trimethoxybenzene; Ar3: Benzene 4-ethenyl-1,2-dimethoxy; Ar4: Benzoic acid, 4-methoxy, methyl ester; Ar5: Benzaldehyde, 3,4-dimethoxy; Ar6: Benzene, 1,2-dimethoxy-4-(1-propenyl); Ar7: Benzoic acid, 3,4-dimethoxy, methyl ester; Ar8: Benzene 1,2,3-trimethoxy, propenyl; Ar9: Ethanone, 1-(3,4,5-trimethoxyphenyl); Ar10: Benzoic acid, 2,4,5-trimethoxy, methyl ester; Ar11: Dimethyl phthalate; Ar12: Benzene dicarboxylic acid dimethyl ester; Ar13: Benzoic acid methyl ester; Ar14: Propenoic acid, 3-phenyl, methyl ester; Ar15: Propenoic acid, 3-(4-methoxyphenyl); Ar16: Propenoic acid, 3-(3,4-dimethoxyphenyl)).

4.3.2 Laboratory analysis of feed, permeate and concentrate

Feed water, permeate, and cleaning concentrate (backwash, caustic and acidic) were sampled and analyzed. In figure 4.9 the results for feed water are shown.

The concentrations of permeate, backwash concentrate and cleaning concentrate are normalized by the concentration of the component present in the feed water and shown in table 4.2.

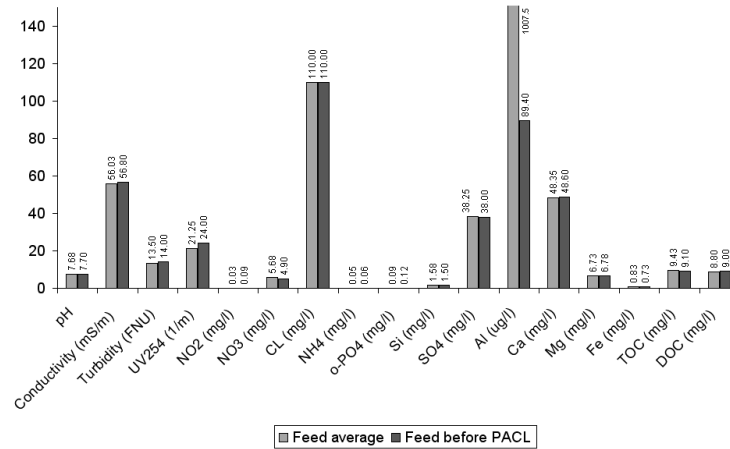


Figure 4.9: Lab. analysis results for feed water before and after coagulant dosing (Poly aluminium chloride).

From the permeate analysis it can be seen that especially turbidity, ortho-phosphate, aluminum and iron are retained on the membrane.

During backwashing, especially turbidity, ortho-phosphate, aluminum and iron are removed from the membrane surface.

From the analysis of acidic- and caustic cleaning concentrate it can be seen that also other components are removed in large quantities, which implies that they were retained on the membrane surface.

For caustic cleaning especially, nitrite, ammonium, silica, aluminum, iron and organic content (DOC and TOC) were removed, while during acidic cleaning ortho-phosphate, aluminum, iron and organic content (UV254) were removed. The high values for conductivity and chlorine can be explained by the high chlorine content of the cleaning agent (Hydrochloric acid) itself.

values for DOC and TOC are twice as high in the caustic cleaning concentrate as found for the feed, implying significant presence of organic content on the membrane surface. Also the increase in values for UV254 during acidic cleaning indicates the presence of organic content.

Aluminum and iron are present on the membrane surface, aluminum is deposited on the membrane surface as it is dosed to the feed water as a flocculant. Also silica is deposited on the membrane surface, most probably as a result of clay- or sand particles present in the feed.

Table 4.2: Normalized analysis results for permeate, backwash concentrate, acidic cleaning concentrate and caustic cleaning concentrate.

	<i>Permeate</i> \times <i>Feed water value</i>	<i>Backwash conc.</i> \times <i>Feed water value</i>	<i>Acidic cleaning conc.</i> \times <i>Feed water value</i>	<i>Caustic cleaning conc.</i> \times <i>Feed water value</i>
pH	1.01	0.99	0.30	1.43
Conductivity (mS/m)	1.00	1.00	6.89	1.67
Turbidity (FNU)	0.06	2.15	0.96	3.41
UV254 (m^{-1})	0.96	1.04	1.74	1.46
Nitrite ($mg.l^{-1}$)	2.08	0.33	0.33	2.00
Nitrate ($mg.l^{-1}$)	0.94	0.98	0.86	0.95
Chlorine ($mg.l^{-1}$)	1.00	1.00	4.73	1.36
Ammonium ($mg.l^{-1}$)	1.00	1.00	1.40	6.80
Ortho-phosphate ($mg.l^{-1}$)	0.56	2.17	9.44	1.56
Silica ($mg.l^{-1}$)	1.00	0.97	1.33	2.35
Sulphate ($mg.l^{-1}$)	0.99	1.02	0.99	1.05
Aluminium ($\mu g.l^{-1}$)	0.10	2.08	7.22	2.02
Calcium ($mg.l^{-1}$)	1.00	1.01	1.01	0.90
Magnesium(mg/l)	1.00	1.01	0.95	0.41
Iron ($mg.l^{-1}$)	0.02	1.76	1.85	3.45
TOC ($mg.l^{-1}$)	0.89	1.17	1.38	1.80
DOC ($mg.l^{-1}$)	0.95	1.14	1.70	1.93

No tests were carried out for microbial content, however, the higher values for nitrite and ammonium indicate that microorganisms might be present on the membrane surface, converting nitrate into nitrite and ammonium according to the nitrogen-cycle.

4.4 Conclusions

The results of the membrane autopsy showed that fouling present on the membrane surface is a complex mixture of polysaccharides, silica, organic industrial or urban waste such as alkyl-benzenes and phthalates and plant materials. The analysis of feed water, permeate, backwash concentrate and cleaning concentrate support these results. Concentrations of indicators of organic content, such as TOC, DOC and UV254 are clearly higher in backwash- and cleaning concentrate. Also iron and silica is found in higher concentrations in the concentrates. Indirect prove for microbial activity is found, as concentrations of nitrite and ammonia are evidently higher in the cleaning concentrates. During caustic cleaning, especially organic content is removed, while during acidic cleaning inorganic content is removed.

Acknowledgements

The author would like to thank Dr. A. Zwijnenburg of the Wetsus Center for sustainable water technology for the SEM footage and Dr. Croué of the Université de Poitiers for the autopsy analysis data.

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